Ecological and economical methods to produce hydrogen for fuel cells

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BASEL - New techniques allow the production of low-cost hydrogen (H2) from renewable energy sources such as ethanol obtained from corn fermentation. The produced H2 can then be used in hydrogen fuel cells that might deliver electricity for applications as different as a car engine or the accumulator of a laptop or cell-phone.

Hydrogen fuel cells have the potential to be a very ecological way of producing energy, because the power is derived from the combination of oxygen (O2) and hydrogen gas molecules (H2) to form water (H2O) as the only waste product. However, providing hydrogen for this chemical reaction has been the ecological caveat for a long time.

Whereas oxygen gas molecules can be easily taken from the air, the classic hydrogen gas production demands a high energy input, normally provided by the combustion of fossil fuels. Therefore, hydrogen fuel cells are only as ecological and economical as the production of the hydrogen used in the reaction.

The energy consuming production of hydrogen has been, and still is, the major point why hydrogen fuel cells are not yet applied on a broad range in everyday use. Recently, however, laboratories headed by Professors L.D. Schmidt and J.R. Salge from Minnesota University developed a method to convert ethanol, or ethanol-water mixtures, directly into H2 by taking advantage of an autothermal reforming process using a rhodium-ceria catalysts.

A catalyst lowers the activation energy of a chemical reaction making it possible to run the reaction at lower temperatures for example. Furthermore, the intrinsic properties of the reaction educts determine which catalyst will work best.

Autothermal reforming, on the other hand, is the production of hydrogen by the combination of partial oxidation, steam reforming, and the water-gas shift in order to obtain a reaction that provides enough heat to drive itself and that generates a maximum amount of hydrogen.

This process combined with the rhodium-ceria catalyst has a large impact on reducing greenhouse gas emissions, because the ethanol used is derived from renewable biomass and the energy is therefore indirectly provided by sunlight through photosynthesis.

Biomass candidates include carbohydrates such as sugar or starch, oils, and crop waste products. Despite this broad range of possibilities, currently ethanol is mainly formed by the fermentation of costly starch. Research, however, suggests that it may also be produced from low-cost crop waste.

Since ethanol is also required as an additive in gasoline fuels in the United States, much effort is being put into research leading towards reliable and cost-effective ethanol production.

To provide the required dependability of a biomass, such as corn, biotech companies are working on producing genetically engineered plants that have enhanced traits such as insect resistance, drought resistance and increased starch levels. All of these traits lead to higher and more constant yields, which in turn allow for a competitive source of ethanol.

Dependable crop yields

Since cultivating dependable amounts of primary biomass products is essential for the success and penetration of the ecologically and economically promising hydrogen fuel cells into everyday use, one would ideally have to create plants that are able to deal with all major environmental concerns.

One of the concerns of biomass products is insect infestation. To resolve the problems that insects can cause, biotech companies have developed transgenic corn varieties, such as YieldGard and Bt corn for example, which provide intrinsic resistance against rootworm and corn borer attacks, and thus reliable crop yields.

A second factor is temperature stress. In fact, temperature stress is one of the major environmental factors that influences the physiological processes of a maturing seed. Thus, if a drought, or a sudden freeze occurs, grain yield and seed weight in many cereal crops such as corn, wheat and barley can be significantly reduced.

Therefore, one target is to create plants surviving at varying temperatures without yield loss. This has in part been achieved by L. Curtis Hannah and his team, who succeeded in altering ADP-glucose pyrophosphorylase, the key enzyme of the starch biosynthetic pathway in maize and potatoes. Due to a mutation in a subunit of the enzyme, the intramolecular interactions were enhanced, which resulted in a higher heat tolerance.

In other experiments with maize, Professor Hannah's team succeeded in finding a mutant called Rev6, which has an increased seed weight (11-18%) compared to wild-type plants. Since Rev6's higher seed weight was not associated with a reduction in seed number, the total seed mass produced by the plant was increased as well. This results in a larger amount of starch production per seed, which in turn increases the cost effectiveness of ethanol.

Improved fuel cells

The first chemical reactor combining oxygen gas molecules with hydrogen gas molecules to form water was developed a long time ago. Nevertheless, hydrogen fuel cells are still being fine-tuned and perfected. Currently, the most used fuel cells are proton exchange membrane fuel cell (PEM).

A PEM is like a sandwich containing a polymer based proton exchange membrane between an anode and a cathode layer. At the anode, a catalyst helps break hydrogen into protons and electrons. While the protons cross the membrane and recombine with oxygen and electrons at the cathode, the electrons travel through an electrical conductor from the anode to the cathode causing a current that can be used to drive an electrical engine, for example.

To improve the overall efficiency, recently, Dr. Suk Won Cha from Stanford University developed new variants of PEM fuel cells. His trick is to use a thinner diffusion layer (electrode) with more, but smaller, channels (20micrometers). The effect is an increased speed of oxygen crossing the electrode, and therefore increased power supply from the fuel cell. This knowledge will be immediately applicable upon small fuel cell applications, thus considerably increasing their efficiency.

Other scientists expressed concerns about this technique, because they feared water molecules might clog the new micro channels. In addressing their concerns, Dr. Cha stated, "I think water clogging is unavoidable as long as the fuel cell operates under 1000C. If a high temperature fuel cell is employed, the improvement from microchannels would be more prominent. However, even at low temperatures smaller channels do improve the performance."

Drawing from observations obtained from recent experiments, Dr. Cha noted, "Microchannels enable the use of an extremely thin gas diffusion layer which improves the performance significantly. So, the combination of microchannels and an extremely thin gas diffusion layer improves the performance significantly regardless of clogging."

Dr. Cha continued, "In my previous experiments, I have used carbon cloth as an electrode which is fairly soft, so it easily conforms to the shape of channels. At that time, the channel clogging effect showed up around 100micrometer channels. However, my recent experiment with carbon paper electrode, which is more rigid, revealed that the clogging effect did not show up at 20micrometer channels. So, if the channels are less clogged by a conformal electrode, the water clogging in channel would be prevented."

Rhodium-ceria catalysts

The new method of producing hydrogen gas molecules by a catalytic partial oxidation on rhodium-ceria catalysts, developed by L.D. Schmidt, J.R. Salge and their research team, provides an ecological and economical hydrogen source. Economical, because the high selectivity and conversion rate helps reducing the required energy input, and ecological, because as Dr. Salge noted, "An ethanol-to-hydrogen process has a closed CO2 loop, as the CO2 produced is used in the growth of the next generation of biomass."

However, the hydrogen produced is not directly usable in currently available proton exchange membrane fuel cells (PEM), because it is not yet pure enough. This means that additional fuel processing, such as preferential CO oxidation (PROX), is necessary to produce hydrogen for current PEM.

Asking Dr. Salge how this process might affect the ecological and economical aspects of hydrogen production from ethanol, he said, "PROX involves an additional air feed before the PROX catalyst, so there should be little effect." Dr. Salge noted that this has been demonstrated by other research groups in the past.

The efficiency of hydrogen production using the rhodium-ceria catalyst suggests that it may be possible to capture >50% of the energy from photosynthesis as electricity. Moreover, the chemical reactions may take place in very small vessels. Dr. Salge comments, "Chemical reactors like this have been tested as small as 0.8 cm in diameter and when used with a fuel cell they produce about 10W."

Thus, the combination of this chemical reactor with a fuel cell may substitute - in only a few years - laptop batteries and cell-phone accumulators. To charge the system, one would simply refuel it with ethanol and remove the wastewater. Scale-ups would make it possible to provide electricity for electrical car engines for example. Dr. Salge added, "We see early use of our system in remote areas where the installation of power lines is not feasible."

In the end, the possibility to grow dependable amounts of biomass that can be used to produce hydrogen in autothermal reforming processes, combined with more efficient fuel cells is making hydrogen fuel cell technology more feasible.